

In the Specification:

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[0009] US Patents Nos. 6,195,252, 6,426,886, 6,466,429, and 6,628,504 disclose EDL capacitors in which a non-polarizable electrode (i.e., the positive electrode) includes an active mass made up of lead dioxide (PbO₂) and lead ~~[sulphate]~~ sulfate (PbSO₄). The electrolyte in these EDL capacitors is contained only in the pores of the electrodes and the separator. There is no free electrolyte within the EDL capacitors since the components are pressed together by reinforcement plates. The pressure provided by the reinforcement plates is necessary to maintain a somewhat reliable contact between the polarizable electrode (i.e., the negative electrode) and the protective layer of the negative electrode current collector.

[0012] According to an aspect of an embodiment of the invention there is provided a positive electrode for use in a Electric Double Layer (EDL) Hybrid Electrochemical Capacitor (HEC), the positive electrode having a lead foil that is punctured serving as a current collector for the positive electrode; and an active mass made up of lead dioxide (PbO₂) and lead ~~[sulphate]~~ sulfate (PbSO₄), wherein the active mass is applied to one or both sides of the lead foil.

[0014] In some embodiments an EDL capacitor according to aspects of an embodiment of the present the present invention includes a current collector for a positive electrode that is made of a lead foil or lead grid onto which (one- or two-sided) a porous active mass is applied. In some embodiments the active mass is made up of a composition of lead dioxide and lead ~~[sulphate]~~ sulfate at different ratios. Reinforcement plates are also included to ensure that the active mass is pressed to the positive electrode current collector. Thus, at prolonged cycling shedding of the active mass from the current collector is avoided by designing the EDL capacitor so that the direction of the lines of electric forces coincide with the direction of the lines of compression forces.

[0019] As another alternative, in other embodiments, the active mass can be prepared from chemical reagents such as lead ~~[sulphate]~~ sulfate (PbO₂) and lead sulphate (PbSO₄) in different ratios. In such embodiments, the ratio between the lead dioxide and the lead ~~[sulphate]~~ sulfate is preferably taken within the range of 1:0.1 to 1:2.5. The ratio is to approximately correspond to the initial state of charge of the negative electrode. For extended cycling of an EDL HEC, it is desirable to start with electrodes having approximately equal state of charge.

[0020] In some embodiments the active mass of the positive electrode can contain one or more dispersed binding agents. In such embodiments it is preferable that the binding agent(s)

employed impart higher durability to the active mass so as to diminish the negative impact of compression on the porosity of the active mass and, thereby, increase cycleability of the electrode and an EDL HEC as a whole. The binding agent(s) can be polymers such as PTFE, PVDF, proton-exchange [~~polyfluorsulphonic~~] polyfluorsulfonic acid of the Nafion type, glass fiber, etc. Moreover, a dispersed porophore, e.g., ammonium bicarbonate, can be added when the active mass of the positive electrode is prepared.

[0032] The electrical components of the EDL HEC include a positive electrode that is made up of an active mass 2 of lead dioxide (PbO₂) and lead [~~sulphate~~] sulfate (PbSO₄) soaked in a suitable electrolyte (not illustrated).

[0033] In some embodiments the electrolyte is advantageously an aqueous solution of [~~sulphuric~~] sulfuric acid. The active mass 2 surrounds a current collector 3. In some embodiments the current collector 3 is made from either lead or a lead based alloy. The co-operative relationship between the active mass 2 and the current collector 3 will be described in further detail below with reference to Figure 2.

[0036] Referring to Figure 2, illustrated is an enlarged cross-sectional view of a positive electrode according to an embodiment of the invention. In particular, the positive electrode includes a punctured lead foil (or lead grid) 11 on which a one or two-sided porous active mass 12 is applied. The lead foil 11 and the active mass 12 shown in Figure 2, correspond to the current collector 3 and active mass 2 shown in Figure 1, respectively. Again, in some embodiments the active mass 12 consists of lead dioxide (PbO₂) and lead [~~sulphate~~] sulfate (PbSO₄) at different ratios. The lead foil 11 can be made in a crimped, wrought or other three-dimensional form with a developed surface.

[0038] The active mass 12 of the positive electrode can contain one or more dispersed binding agents. The binding agent can be a polymer such as PTFE, PVDF, proton-exchange [~~polyfluorsulphonic~~] polyfluorsulfonic acid of the Nafion type, or glass fiber. Moreover, a dispersed porophore, e.g., ammonium bicarbonate, can be added when the active mass 12 is prepared. If the porophores are added to the active mass 12, they are removed in another manufacturing step by heating the entire active mass 12 to an appropriate temperature. Moreover, the preparation of the positive electrode includes a uniform application of the active mass 12 on one or both sides of the lead foil 11, pressing, and sintering at elevated temperatures.

[0052] The initial active mass 12 was made from a paste of 4PbO□PbSO₄, which is widely used for formation of positive plates in lead-acid batteries. Proton-exchange

[polyfluorsulphonic] polyfluorsulfonic acid of Nafion type was added as a binding agent (2%) as well as 3% of finely cut separator of Grace type. The paste was applied on both sides of the punctured lead foil 11 at total amount of 0.5 g/cm². It was directly formed within the EDL HEC (refer to Figure1). The formation was carried out in 10% sulfuric acid to which 0.5 % of phosphoric acid was added. The pressure did not exceed 1 kg/cm². Porosity of the electrodes after formation amounted to 60%.

[0053] The electrolyte was then concentrated to 35% of [sulphuric] sulfuric acid and the cell was compressed with 5 kg/cm². Two negative electrodes 1 made of activated carbon ADG with specific surface of 1150 m²/g were used. Layers of the dense rubber gaskets 8 were placed on the backside of the metal layers 5 of the current collector for shock absorption. A 0.5 mm thick AGM type separator was used, 65% of its pores being flooded with electrolyte. The pores of the negative electrode 1 were flooded to 71%. Current density of 0.1 A/g was used. The EDL HEC was cycled within the range of 0.6 to 2.2 V. The average specific capacity obtained was 0.092 Ah per gram active mass, which is 40.1% of the theoretical. The EDL HEC reached 6930 cycles before failure.